



COMPREHENSIVE CHIROPTICAL SPECTROSCOPY

Instrumentation, Methodologies, and
Theoretical Simulations

VOLUME ONE

EDITED BY

NINA BEROVA • PRASAD L. POLAVARAPU
KOJI NAKANISHI • ROBERT W. WOODY

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COMPREHENSIVE CHIROPTICAL SPECTROSCOPY

Volume 1

PREFACE

Chirality is a phenomenon that is manifested throughout the natural world, ranging from fundamental particles through the realm of molecules and biological organisms to spiral galaxies. Thus, chirality is of interest to physicists, chemists, biologists, and astronomers. Chiroptical spectroscopy utilizes the differential response of chiral objects to circularly polarized electromagnetic radiation. Applications of chiroptical spectroscopy are widespread in chemistry, biochemistry, biology, and physics. It is indispensable for stereochemical elucidation of organic and inorganic molecules. Nearly all biomolecules and natural products are chiral, as are the majority of drugs. This has led to crucial applications of chiroptical spectroscopy ranging from the study of protein folding to characterization of small molecules, pharmaceuticals, and nucleic acids.

The first chiroptical phenomenon to be observed was optical rotation (OR) and its wavelength dependence, namely, optical rotatory dispersion (ORD), in the early nineteenth century. Circular dichroism associated with electronic transitions (ECD), currently the most widely used chiroptical method, was discovered in the mid-nineteenth century, and its relationship to ORD and absorption was elucidated at the end of the nineteenth century. Circularly polarized luminescence (CPL) from chiral crystals was observed in the 1940s. The introduction of commercial instrumentation for measuring ORD in the 1950s and ECD in the 1960s led to a rapid expansion of applications of these forms of chiroptical spectroscopy to various branches of science, and especially to organic and inorganic chemistry and to biochemistry.

Until the 1970s, chiroptical spectroscopy was confined to the study of electronic transitions, but vibrational transitions became accessible with the development of vibrational circular dichroism (VCD) and Raman optical activity (ROA). Other major extensions of chiroptical spectroscopy include differential ionization of chiral molecules by circularly polarized light (photoelectron CD), measurement of optical activity in the X-ray region, magnetochiral dichroism, and nonlinear forms of chiroptical spectroscopy.

The theory of chiroptical spectroscopy also goes back many years, but has recently made spectacular advances. Classical theories of optical activity were formulated in the early twentieth century, and the quantum mechanical theory of optical rotation was described in 1929. Approximate formulations of the quantum mechanical models were developed in the 1930s and more extensively with the growth of experimental ORD and ECD studies, starting in the late 1950s. The quantum mechanical methods for calculations of chiroptical spectroscopic properties reached a mature stage in the 1980s and 1990s. *Ab initio* calculations of VCD, ECD, ORD, and ROA have proven highly successful and are now widely used for small and medium-sized molecules.

Many books have been published on ORD, ECD, and VCD/ROA. The present two volumes are the first comprehensive treatise covering the whole field of chiroptical spectroscopy. Volume 1 covers the instrumentation, methodologies, and theoretical simulations for different chiroptical spectroscopic methods. In addition to an extensive

treatment of ECD, VCD, and ROA, this volume includes chapters on ORD, CPL, photoelectron CD, X-ray-detected CD, magnetochiral dichroism, and nonlinear chiroptical spectroscopy. Chapters on the related techniques of linear dichroism, chiroptical imaging of crystals and electro-optic absorption, which sometimes supplement chiroptical interpretations, are also included. The coverage of theoretical methods is also extensive, including simulation of ECD, ORD, VCD, and ROA spectra of molecules ranging from small molecules to macromolecules. Volume 2 describes applications of ECD, VCD, and ROA in the stereochemical analysis of organic and inorganic compounds and to biomolecules such as natural products, proteins, and nucleic acids. The roles of chiroptical methods in the study of drug mechanisms and drug discovery are described.

Thus, this work is unique in presenting an extensive coverage of the instrumentation and techniques of chiroptical spectroscopy, theoretical methods and simulation of chiroptical spectra, and applications of chiroptical spectroscopy in inorganic and organic chemistry, biochemistry, and drug discovery. In each of these areas, leading experts have provided the background needed for beginners, such as undergraduates and graduate students, and a state-of-the-art treatment for active researchers in academia and industry.

We are grateful to the contributors to these two volumes who kindly accepted our invitations to contribute and who have met the challenges of presenting accessible, up-to-date treatments of their assigned topics in a timely fashion.

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PART I

INTRODUCTION

ON THE INTERACTION OF LIGHT WITH MOLECULES: PATHWAYS TO THE THEORETICAL INTERPRETATION OF CHIROPTICAL PHENOMENA

Georges H. Wagnière

1.1. A BRIEF HISTORICAL RETROSPECTIVE

1.1.1. On the Nature of Light

The ancient Greek philosophers, such as Pythagoras and his disciples, later also Euclid, gave early speculations on the nature of light. Yet the fundamental question, what light really is, has been systematically approached only following the birth of modern astronomy in the fifteenth and sixteenth century. The developing manufacture of lenses and of other optical components for technical purposes undoubtedly stimulated this scientific endeavor.

The lasting foundations of a modern theory of light were, however, not laid before the second half of the seventeenth century. While Isaac Newton (1642–1727), after discovering the spectral resolution of white light, tended to consider it as made up of particles, Christiaan Huygens (1629–1695) attributed to it a wave nature and thereby succeeded in explaining reflection and refraction. Significant advances in the understanding of light were accomplished in the nineteenth century. Augustin Fresnel (1788–1827) extended the theory of Huygens to explain diffraction, thereby affirming the apparent superiority of the wave model. However, a satisfying deeper explanation of the nature of the oscillating medium was still missing.

Not before the development of a theory of electricity and magnetism was a significant next step made forward. Jean-Baptiste Biot (1774–1862) not only made important contributions to the understanding of the relation between an electric current and a magnetic field—the Biot–Savart law—but also discovered the rotation of the plane of linearly

polarized light in "optically active" liquids, such as sugar solutions. Michael Faraday (1791–1867) discovered both (a) the electromagnetic law of induction and (b) the effect named after him, namely, that a magnetic field could cause optical rotation in a material medium. James Clerk Maxwell (1831–1879) subsequently succeeded in mathematically unifying the laws of electricity and magnetism. From Maxwell's equations (see Section 1.2.1) one may directly derive an electromagnetic wave equation that has proven to be an excellent description of the properties of light and its propagation. Light then appears as a *transverse wave*, with an *electric* and a *magnetic* field component perpendicular to each other and to the direction of propagation.

Unexpectedly, and in spite of the success of the classical wave theory, the concept of a particle nature of light, dormant for about two centuries, resurfaced at the beginning of the twentieth century. In order to satisfactorily interpret the law of blackbody radiation, Max Planck (1858–1947) was led to assume that an electromagnetic field inside a cavity, and in thermal equilibrium with it, behaves as a collection of harmonic oscillators, the energy of which is quantized. From the photoelectric effect, Albert Einstein (1879–1955) concluded that radiation is absorbed by an atom in the form of quanta of energy proportional to its frequency, $E = h\nu$, where the quantity h is Planck's constant. Thus the concept of the *photon* was born. The particle-wave duality, not only for light, but also for matter, became a cornerstone of the quantum mechanics that then soon developed.

Assuming a formal analogy between the radiation oscillators and the quantum mechanical harmonic oscillator, P. A. M. Dirac (1902–1984) initiated an algebra of photon states. The radiation field is consequently represented as a many-photon system, each photon acting as a harmonic oscillator of given frequency. State changes of the radiation field are then described by photon creation and annihilation operators. However, even in this quantized frame, the electromagnetic picture derived from the classical description is essentially maintained. Considering a classical ray of light, one may, according to how the electric and magnetic field oscillate in space and time, speak of *linear*, *circular*, or *elliptic polarization*. The concept of *polarization* may also be attributed to a *single photon*. Beth's experiment in 1936 revealed that circularly polarized light carries angular momentum, and that this angular momentum corresponds to a *spin of the photon* of $\pm 1\hbar$, depending on if the photon is *left* or *right* circularly polarized.

In our aim to describe chiroptical phenomena of molecules, we ask ourselves to what extent the quantization of the radiation field must be taken into account. Is it for our purposes sufficient to describe the electromagnetic field classically, or is it also necessary to explicitly consider this field quantization? A fact taught in elementary quantum mechanics courses is that the quantum mechanical harmonic oscillator for increasing quantum numbers behaves more and more like a classical oscillator. Similarly, the radiation field at high quantum numbers, corresponding to a high photon density, behaves more and more classically as the intensity grows.

One of Albert Einstein's numerous seminal contributions to modern physics was to recognize that *absorption* of light by matter obviously can only be electromagnetic field-induced, but that there are two kinds of *emission*, *spontaneous* and *induced*. Spontaneous emission occurs even in the absence of external radiation. It may be pictured as an excitation of the vacuum state of the electromagnetic field by the atom or molecule. Its detailed interpretation indeed requires field quantization. In absorption and induced emission, on the other hand, one must assume a certain external light intensity to be present, and therefore the classical description is admissible. This is indeed the point of view that we shall adopt.

The particular practical significance of *induced emission* only became apparent in the middle of the last century and led to the development of *masers and lasers*. Some of the chiroptical phenomena that we shall briefly consider in the following sections indeed require the use of lasers. We shall treat these effects in the frame of the so-called semiclassical radiation theory [1–6].

1.1.2. Quantum Chemistry in Its Early Stages

For the understanding of the atomic and molecular spectra, measured at higher and higher resolution in the late nineteenth and early twentieth century, it became clear that only a quantum mechanical description of matter would be satisfactory. This also initiated the special field of *quantum chemistry*. Even the simplest molecule, that of hydrogen, already poses some difficult problems, however. In the calculation of Heitler and London [7], a solution of the Schrödinger equation for the electrons is sought, while a priori keeping the nuclei fixed. A systematic investigation of the *separability* of *electronic* and *nuclear motion* was worked out by Born and Oppenheimer [8]. They showed that due to the mass difference between electrons and nuclei, the molecular Schrödinger equation may be approximately separated into an equation for the electrons at different fixed nuclear positions, and an equation for the vibrations of the nuclei in the potential energy surfaces that are derived from the solutions of the electronic equation. Finally, there is the rotation of the molecule as a whole to be considered, approximated by a three-dimensional rotator, or top, of appropriate symmetry. Consequently, the overall molecular wavefunction may then be represented as a product:

$$\Psi_{\text{molec}} = \Phi_{\text{el}} X_{\text{vib}} \Theta_{\text{rot}},$$

and the energy E can be expressed as a sum. A molecular change of state is correspondingly written as

$$\Delta E_{\text{molec}} = \Delta E_{\text{el}} + \Delta E_{\text{vib}} + \Delta E_{\text{rot}},$$

with ΔE_{el} usually on the order of 10^4 – 10^5 cm^{-1} , $\Delta E_{\text{vib}} \approx 10^2$ – 10^3 cm^{-1} , $\Delta E_{\text{rot}} \approx 10^{-1}$ – 10^1 cm^{-1} .

It was soon recognized that the solution of the electronic equation alone already is a formidable task, the main difficulty being the electron–electron interaction. A general and rigorously justifiable procedure was then developed, consisting of several steps. (a) Calculate a set of orthonormalized molecular one-electron functions—for instance, *molecular orbitals* (MO) as linear combinations of *atomic orbitals* (LCAO)—by solving a simplified electronic Schrödinger equation that neglects electron–electron interaction. Multiply each MO with an appropriate spin function. Assign the electrons individually to these *spin orbitals*, respecting the *Pauli exclusion principle*. (b) Such an assignment was given the name *configuration*. An electron configuration is thus described as a product of the occupied one-electron molecular spin orbitals. Because electrons are fermions, these products must be antisymmetric with respect to the interchange of any two electrons. Therefore, the many-electron functions are to be *antisymmetrized* and may be written in the form of *Slater determinants*. Every Slater determinant thus represents an *electron configuration*. The solution of the many-electron Schrödinger equation is performed on the basis of these antisymmetrized configurational functions and is termed *configuration interaction* (CI). The electronic wavefunctions finally so obtained consequently present themselves as linear combinations of such Slater determinants.